

# Direct measurement of three-body interactions

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Three-body interactions have been measured among three charged colloidal particles in deionized solvent. Two of the particles have been confined to an optical line-trap while the third one was approached by means of a focused laser beam. The experimentally determined three-body interactions are attractive and roughly of the same magnitude and range as the pair-interactions. In addition, numerical calculations have been performed, which show good agreement with the experimental results.

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Precise knowledge of particle interactions is of utmost importance for the understanding of thermodynamic properties of condensed matter. We typically treat interactions in a pair-wise fashion, but if the governing physical equations are non-linear, interactions between two particles can be modified by a close third or fourth particle. The total energy is then no longer given by the sum of all pair-potentials but additional many-body interactions appear. Physical examples of many-body interactions are abundant: inter atomic potentials, electron screening in metals [1], island formation on surfaces [2], chemical processes in solids [3] and even noble gases which possess a closed-shell electronic structure [4, 5]. In view of its general importance it seems surprising that until now no direct measurement of many-body interactions has been performed, however, it is hard to imagine that such a measurement could be performed in an atomic system, where positional information is provided in an integrated form, i.e. by structure factors or pair-correlation functions. Many-body interactions can be directly evaluated only when the positional information is provided, i.e. the particles' trajectories in space and time are known.

In contrast to atomic systems, length- and time-scales in colloidal systems are accessible with optical experiments and it is possible to obtain individual particle trajectories. Additionally, colloidal interactions can be tuned over a wide range, simply by changing the salt concentration (in contrast to atoms where interactions are unchangeably dictated by their electronic structure). At sufficiently small salt concentrations, the interaction range can reach several  $\mu\text{m}$ . If more than two colloids are within this range, a simple pair-wise description breaks down and many-body interactions occur. Indeed, three-body effects have been found in recent computer simulations [6, 7, 8]. It was also demonstrated by experiments [9] and simulations [10, 11], that the effective pair-potential of a two-dimensional colloidal liquid shows a density dependence, hinting towards many-body effects. Accordingly, colloidal suspensions represent an ideal model system for systematic investigations in this field.

Here we present the first direct measurement of

three-body interactions in a suspension of charged colloidal particles. Two of the particles were confined by means of a scanned laser tweezer to a quasi-static line-shaped optical trap where they diffused due to thermal fluctuations. A third particle was localized in a point-like laser tweezer at distance  $d$  (see inset of Fig.1). When the third particle was approached to the line trap, significant deviations from pairwise additivity have been observed. This experimental finding is also supported by the additionally performed Poisson-Boltzmann calculations.

We used a highly diluted aqueous suspension of charge-stabilized silica spheres (990nm diameter), which has been confined in a silica glass cuvette with  $200\mu\text{m}$  spacing. The cuvette was connected to a standard deionization circuit described elsewhere [12]. Before each measurement the water was pumped through the ion exchanger and typical ionic conductivities below  $0.07\mu\text{S}/\text{cm}$  were obtained. After the suspension was injected, the cuvette was disconnected from the circuit during the measurements. This procedure yielded stable and reproducible ionic conditions during the experiments.

Particle interaction measurements performed with scanned optical tweezers have been reported by several other groups [13, 14], therefore the technique is here only briefly described. The focussed beam of an  $\text{Ar}^+$  laser (488nm) was scanned across our sample cell by means of a galvanostatically driven mirror with a frequency of about 350 Hz. This yielded a Gaussian intensity distribution along and perpendicular to the scanning direction with halfwidths  $\sigma_x \approx 4.5\mu\text{m}$  and  $\sigma_y \approx 0.5\mu\text{m}$ , respectively. Due to the negatively charged silica substrate, the particles experience a repulsive vertical force balanced by the particle weight and the vertical component of the light force. The potential in the vertical direction is much steeper than the in-plane laser potential, therefore vertical particle fluctuations can be disregarded. The particles were imaged with a long-distance, high numerical aperture microscope objective onto a CCD camera and the lateral positions of the particle centers were determined with a resolution of about 25 nm by a particle recognition algorithm.

We first inserted a single particle into the trap where it diffused due to thermal fluctuations. From the positional probability distribution  $P(x, y)$ , the laser potential  $u_L(x, y)$  is directly obtained via the Boltzmann distribution  $P(x, y) \propto e^{-\beta u_L(x, y)}$ , where  $\beta^{-1}$  corresponds to the thermal energy of the suspension. Next, we inserted a second particle in the trap. The four-dimensional probability distribution is now  $P(x_1, y_1, x_2, y_2) = P_{12} e^{\beta(u_L(x_1, y_1) + u_L(x_2, y_2) + U(r))}$  with  $x_i, y_i$  being the position of the  $i$ -th particle relative to the laser potential minimum and  $U(r)$  the distance dependent pair-interaction potential between the particles. Since it is reasonable to assume that the pair interaction depends only on the particle distance, we projected  $P(x_1, y_1, x_2, y_2)$  onto a one-dimensional distance distribution  $P(r)$ . From the measured  $P(r)$  we obtained the total potential energy of the particles and after subtracting the external potential we were left with the pair interaction potential  $U(r)$ .

The pair-interaction potential of two charge-stabilized particles in the bulk is theoretically predicted [15, 16] to correspond to a Yukawa potential

$$\beta U(r) \equiv \beta u_{12}(r) = (Z^*)^2 \lambda_B \left( \frac{\exp(\kappa R)}{1 + \kappa R} \right)^2 \frac{\exp(-\kappa r)}{r} \quad (1)$$

where  $Z^*$  is the renormalized charge [17] of the particles,  $\lambda_B$  the Bjerrum-length (in water at room temperature),  $\kappa^{-1}$  the Debye screening length (given by the salt concentration),  $R$  the particle radius and  $r$  the center-center distance of the particles. Fig.2 shows the experimentally determined pair-potential (symbols) together with a fit to Eq.(1) (solid line). As can be seen, our data are well described by Eq.(1). As fitting parameters we obtained  $Z^* \approx 6500$  electron charges and  $\kappa^{-1} \approx 470\text{nm}$ , respectively.  $Z^*$  is in good agreement with the predicted value of the saturated effective charge of our particles [18, 19] and  $\kappa^{-1}$  agrees reasonably with the bulk salt concentration in our suspension as obtained from the ionic conductivity. Given the additional presence of a charged substrate, it might seem surprising that Eq.(1) describes our data successfully. However, it has been demonstrated experimentally [20] and theoretically [21, 22] that a Yukawa-potential captures the leading order interaction also for colloids close to a charged wall. A single confining wall introduces only a very weak (below  $0.1k_B T$ ) correction due to additional dipole repulsion which is below our experimental resolution. Repeating two-body measurements with different laser intensities (50mW to 600mW) yielded within our experimental resolution identical pair potential parameters. This also demonstrates that possible light-induced particle interactions (e.g. optical binding [23]) are negligible.

Finally, we approached a third particle by means of an additional laser trap at distance  $d$  (cf. Fig.1) where it

was localized during the whole measurement. We carefully checked that the empty laser trap (i.e. without the third particle) has no influence on the pair-interaction potential on the particles in the line tweezer. From the distance distribution of the two particles in the laser trap, we can, applying the same procedure as in the two particle measurement, extract the total interaction energy which is now also characterized by the distance  $d$ , i.e.  $U = U(r; d)$ . Following the definition of McMillan and Mayer [24], the total interaction energy for three particles  $U(r; d)$  can be written as

$$U(r; d) = u_{12}(r_{12}) + u_{13}(r_{13}) + u_{23}(r_{23}) + u_{123}(r_{12}, r_{13}, r_{23}) \quad (2)$$

with  $u_{ij}$  being the pair-potential between particles  $i$  and  $j$  as shown in Fig.2 and  $u_{123}$  the three-body interaction potential.  $r_{12}$ ,  $r_{23}$  and  $r_{13}$  are the distances between the three particles which can - due to the chosen symmetric configuration - be expressed by the two variables  $r = r_{12}$  and  $d$ .

The measured interaction energies  $U(r; d)$  are plotted as symbols in Fig.3 for several distances of the third particle ( $d = 4.1, 3.1, 2.5, 1.6\mu\text{m}$ ). As expected,  $U(r; d)$  becomes larger as  $d$  decreases due to the additional repulsion between the two particles in the trap and the third particle. In order to test whether the interaction potential can be understood in terms of a pure superposition of pair-interactions, we first calculated  $U(r; d)$  according to Eq.(2) with  $u_{123} = 0$ . This was easily achieved because the positions of all three particles were determined during the experiment and the distance-dependent pair-potential is known from the two-particle measurement described above (Fig.2). The results are plotted as dashed lines in Fig.3. Considerable deviations from the experimental data can be observed, in particular at smaller  $d$ . These deviations can only be explained, if we take three-body interactions into account. Obviously, at the largest distance, i.e.  $d = 4.1\mu\text{m}$  our data are well described by a sum over pair-potentials which is not surprising, since the third particle cannot influence the interaction between the other two, if it is far enough from both. In agreement with theoretical predictions [8], the three-body interactions therefore decrease with increasing distance  $d$ .

According to Eq.2 the three-body interaction potential is simply given by the difference between the measured  $U(r, d)$  and the sum of the pair-potentials (i.e. by the difference between the measured data and their corresponding lines in Fig.3). The results are plotted as symbols in Fig.4. It is seen, that  $u_{123}$  is entirely attractive and becomes stronger as the third particle is approached. The range of  $u_{123}$  is of the same order as the pair-interaction potentials. To support our results, we also performed Poisson-Boltzmann (PB) calculations, in a similar way as in [8]. The PB theory provides a mean-field description in which the micro-ions in the

solvent are treated as a continuum, neglecting correlation effects between the micro-ions. It has repeatedly been demonstrated [25, 26] that in case of monovalent micro-ions the PB theory provides a reliable description of colloidal interactions. We used the multi-centered technique, described and tested in other studies [10, 11] to solve the non-linear PB equation for the electrostatic mean-field potential  $\Phi$ , which is related to the micro ionic charge density  $\rho_c = -(\kappa^2/4\pi\lambda_B)\sinh\Phi$ . Integrating the stress tensor, depending on  $\Phi$ , over a surface enclosing one particle, results in the force acting on this particle. Calculating the force  $f_{12}$  and from it the pair-potential between only two particles, we first reproduced the measured pair-interaction in Fig.2. The calculation of three-body potentials was then carried out by calculating the total force acting on one particle in the line trap (say, particle 1) and subtracting the corresponding pair-forces  $f_{12}$  and  $f_{13}$  obtained previously in the two-particle calculation. The difference has been integrated to obtain the three-body potential. The results are plotted as lines in Fig.4 and show reasonable agreement with the experimental data (in particular with respect to the range and size of  $u_{123}$ ). This strongly supports our interpretation of the experimental results in terms of three-body interactions. The remaining deviations between theory and experiment are probably due to small variations in salt concentration but may also be due to small differences in the size and surface charge of the colloidal particles used in the experiment, which have been assumed to be identical in the PB calculations.

We have demonstrated that in case of three colloidal particles, three-body interactions present a considerable contribution to the total interaction energy and must therefore inevitably be taken into account. Whenever dealing with systems comprised of many (much more than three) particles, in principle also higher-order terms have to be considered. We expect, however, that there is an intermediate density regime, where the macroscopic properties of systems can be success-

fully described by taking into account only two- and three-body interactions. Indeed, there are systems where this was experimentally observed [2, 5]. At even larger particle densities  $n$ -body terms with  $n > 3$  have to be additionally considered, which may partially compensate. Even in this regime, however, many-body effects are not cancelled, but lead to notable effects, e.g. to a shift of the melting line in colloidal suspensions, as recently demonstrated by PB calculations [10, 11].

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## I. FIGURE CAPTIONS

*Figure 1* Photograph of sample cell with two silica particles confined to a light trap created by an optical tweezers and a third particle trapped in a focused laser beam. The inset shows schematically the experimental geometry.

*Figure 2* Measured pair-interaction potentials  $U(r)$  (symbols) in the absence of the third particle. The data agree well with a Yukawa potential (solid line). In the inset the potential is multiplied by  $r$  and plotted logarithmically, so that Eq. 1 transforms into a straight line.

*Figure 3* Experimentally determined interaction energy  $U(r)$  (symbols) for two particles in a line tweezers in the presence of a fixed third particle with distance  $d$  on the perpendicular bisector of the line trap. For comparison the superposition of three pair-potentials is plotted as lines. Symbols and lines are labeled by the value of  $d$ .

*Figure 4* Three-body potentials for different  $d$ . Measured three-body potentials indicated by symbols. The lines are three-body potentials as obtained from the solutions of the nonlinear Poisson-Boltzmann equation for three colloids arranged as in the experiment. The parameters in the Poisson-Boltzmann calculation were chosen so that the pair-interaction potentials were correctly reproduced. Symbols and lines are labeled by the value of  $d$ .

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